Photoinitiated emulsion polymerization of styrene or methyl methacrylate in the presence of zinc oxide

I. HUDEC, D. MIKULÁŠOVÁ, P. CITOVICKÝ, and V. CHRÁSTOVÁ

Department of Chemical Technology of Plastics and Fibres,
Slovak Technical University, CS-812 37 Bratislava

Dedicated to Professor RNDr. J. Gašperík, founder of the Department of Organic Technology and of the Department of Chemical Technology of Plastics and Fibres of the Slovak Technical University on the occasion of the 40th anniversary of their foundation

It is suitable to use visible light for the photoinitiated emulsion polymerization of styrene or methyl methacrylate in the presence of zinc oxide and 3,6-diaza-1,8-octanediamine at 30 °C.

The conversion curves of styrene or methyl methacrylate polymerization are characterized by an induction period, which is greater in the case of the polymerization of methyl methacrylate. The higher the concentration of zinc oxide the higher the induction period. The effect of postpolymerization was observed, which is more expressive at higher concentration of ZnO.

Some molecular characteristics of the obtained polystyrene and poly(methyl methacrylate) were determined by means of viscosimetric and GPC methods. The determined values of the relative molecular mass of polystyrene were in the range of 8.5×10^6 to 2.9×10^7, the coefficient of polymolecularity was in the range 1.3 to 1.5. The relative molecular mass for poly(methyl methacrylate) was in the range of 1.0×10^7 to 2.4×10^7 with the lowest value for the coefficient of polymolecularity 1.42.

Для фотохимической эмульсионной полимеризации стирола и метилметакрилата в присутствии оксида цинка и 3,6-диаза-1,8-октандиамина при температуре 30 °C подходит видимый свет.

Кривые превращения при полимеризации стирола и также метилметакрилата характеризуются индукционным периодом, который в случае полимеризации метилметакрилата тем больше, чем выше концентрация оксида цинка. Наблюдалось явление после-полимеризации, которое выражено сильнее при более высокой концентрации оксида цинка.

Методами вискозиметрии и гелевой хроматографии были определены некоторые молекулярные характеристики образующегося полистирола

и полиметилметакрилата. Определенные данные $\bar{M}_{r,w}$ полистирола были в интервале $8{,}5 \cdot 10^6$—$2{,}9 \cdot 10^7$ с коэффициентом полимолекулярности в интервале 1,3—1,5, а у полиметилметакрилата значения $\bar{M}_{r,w}$ составляли $1{,}0 \cdot 10^7$—$2{,}4 \cdot 10^7$ с самым низким значением коэффициента полимолекулярности 1,42.

In paper [1] was verified the possibility to use ZnO as a heterogeneous photosensibilizer in the region of visible light for the emulsion polymerization of methyl methacrylate. The authors [2] were dealing with the problem of methyl methacrylate polymerization in the presence of an aqueous suspension of ZnO and by using u.v. light. They have considered that the photoinitiator itself was formed on the surface of ZnO and that it was a certain form of oxygen. Because under the conditions used by the authors the styrene polymerization did not take place, they assumed that photoactivated oxygen should have an anionic character $^{\bullet}O_2^-$.

Yamamoto and *Oster* [3] used zinc oxide and u.v. light in the presence of traces of water and oxygen for the polymerization of some vinyl monomers. But they obtained relatively low conversions of monomer.

The photosensibilizing effect of substances, which form the heterogeneous component of the polymerization system, was also used for the grafting of polymers, for instance, by the grafting of various kinds of fibres with methyl methacrylate in the presence of traces of oxygen and some metal oxides in the form of water dispersions [4]. The authors of the paper considered that from the view-point of the photochemical reaction the character of the oxides as semiconductors is important; the photoexcited electrons migrating on the solid surface can reduce the adsorbed oxygen and so form initiation centres for the consecutive polymerization.

Hitherto the emulsion polymerization with a heterogeneous photosensibilizer has not been studied. The emulsion polymerization with a heterogeneous initiator, whether of organic character (powdered low-oxidized polypropylene, polyethylene or poly(vinyl chloride) [5, 6]), or of inorganic character (synthetic zeolites, metal oxides [1]) was studied. In most cases the polymerization system had to contain also an activator of initiation, and that either a two-component one — FeSO₄ with bisodium salt of ethylenediaminetetraacetic acid, or a one-component one — 3,6-diaza-1,8-octanediamine.

Polystyrene prepared with heterogeneous initiator had a high relative molecular mass (of the order 10^6—10^7) and a relatively low polymolecularity [7]. According to the sophistication of the polymerization system used and the interesting molecular mass characteristics of the polymers formed, the photoinitiated polymerization of styrene and methyl methacrylate was topical mainly from the view-point of developing the findings of polymerization in a multicomponent system.

Experimental

Chemicals

Components of the polymerization system: methyl methacrylate (MMA) and styrene (S) as monomers, Slovasol 2430 as nonionic emulsifier, 3,6-diaza-1,8-octanediamine (TETA) as activator, zinc oxide, water and nitrogen, used as inert atmosphere, were purified in the same manner as mentioned in paper [1].

Methyl ethyl ketone, anal. grade (dried over $CaCl_2$), methanol, anal. grade (water traces removed with powdered magnesium using iodine as catalyst).

Procedures

The styrene polymerization was carried out in glass ampoules as mentioned in paper [1]. The separation of the polymer from the emulsion and the procedure for the consecutive processing is also stated in paper [1]. Unlike the styrene polymerization, which took place in daylight, the methyl methacrylate polymerization was carried out using a 250 W mercury lamp as a source of cold light in the visible region. (The use of u.v. light was not advantageous for the polymerization.) In order to ensure controlled light conditions the ampoules after weighing of zinc oxide were wrapped in an aluminium foil, which was removed only after filling, sealing, and shaking the ampoule. Then the ampoule was inserted into a rotating frame in a dark thermostat with a light source. The possibility of the influence of secondary light effects was eliminated by a blank test. The bath was tempered at 30 °C. The composition of the polymerization system used is in Table 1.

Table 1

Composition of the polymerization system

Component	Quantity in ampoules	Concentration mol dm_{cm}^{-3}
Zinc oxide	0.4 g	2.73×10^{-1}
	0.1 g	6.66×10^{-2}
TETA (solution)	0.5 ml	1.66×10^{-3}
Slovasol 2430 (solution)	7.0 mol	2.70×10^{-2}
Water	7.5 ml	
Methyl methacrylate	3.0 ml	1.55

After completion of the polymerization the prepared polymer was precipitated by pouring the content of the ampoule (by steady stirring) into 500 cm³ of methanol containing 10 cm³ of concentrated HCl.

Gel permeation chromatography (GPC)

The measurings were carried out with the chromatograph Waters Ass., ALC/GPC 501 with a four-column system, which comprised three columns packed with styrene—divinyl benzene gel Styragel (with the nominal porosity of the gel packing 5×10^5, 10^5, 10^4 nm) and one column packed with inorganic gel on the basis of SiO_2 of the type Merckogel SI 5000 (application range 10^5—2.5×10^7). The GPC device was temperated by air at 25 °C.

A two-component solvent methyl ethyl ketone—methanol in the volume ratio 89:11 was used. The concentration used for polystyrene and poly(methyl methacrylate) was 2 mg cm^{-3}, the injection time was 2 min and the rate of elution was kept constant at 1 cm^3 min^{-1}. The volume of the overflowed solvent was measured by a siphon (count = 3.75 cm^{-3}). The signal from the differential refractometer with the impulse of the volumetric detector was registered by the device TZ 21 S and PM 2000.

The arrangement was calibrated by a set of polystyrene standards. The maximum (peak) of the detected chromatographic wave was considered to be the elution volume of the corresponding standard. From the values of the elution volume V_e obtained and from the known values of the relative molecular mass of the standards the calibration dependence $\log M_p = f(V_e)$ was calculated, which is illustrated by the polynom of the first order in the form

$$\log M_p = 13.1404 - 0.1823 \ V_e$$

The calibration dependence was linear in the range of the relative molecular mass $(2.0 \times 10^5$—$2.1 \times 10^7)$. The coefficient of the linear correlation, used as the criterion of adequacy of the theoretical equation and of the experimental values $r_{y.x}^2$, was 0.9892. By evaluating the results obtained from measuring the poly(methyl methacrylate) samples, the universal calibration dependence [8] was used for the calibration of the device

$$\log [\eta] \ \bar{M} = f(V_e)$$

the course of which is illustrated by the polynom of the first order in the form

$$\log ([\eta] \ \bar{M} \ \text{cm}^{-3} \ \text{mol}) = 15.263237 - 0.242587 \ V_e/\text{count}$$

which was obtained by means of a set of polystyrene standards.

The correction on the broadening effect was made mathematically on the basis of *Tung's* integral equation [9]. The procedure mentioned in papers [10—12] was used for the determination of the resolution factor h on the elution volume.

For the calculation on the corrected mean of the relative molecular mass *Chang* and *Huang's* iteration program was used [13].

Viscosimetry

For the determination of the limiting viscosity number of poly(methyl methacrylate) samples Ubbelohde's viscosimeter was used. Methyl ethyl ketone—methanol was used as solvent in the ratio 89:11 at 25 °C. The mixed solvent used for measuring the molecular

488

characteristics of poly(methyl methacrylate) and polystyrene represents a mixture near to the theta solvent for polystyrene [14] (a mixture of MEK and MeOH in the ratio 88.7 : 11.3 at 25 °C). A small excess of methyl ethyl ketone had to ensure the stability of the solution of polystyrene samples at lower temperatures than those used in measuring. For poly(methyl methacrylate) the composition of the theta mixture methyl ethyl ketone—methanol corresponds to the volume ratio 66.2 : 33.8 at 25 °C (determined turbidimetrically). Because in the available literature there has not yet been published any common theta solvent for polystyrene and poly(methyl methacrylate), the above-mentioned composition of the solvent mixture was chosen which actually represents a bad solvent for poly(methyl methacrylate) and, for polystyrene, a solvent which is very near to the theta solvent. According to the very high relative molecular mass of the polymer the starting mass concentration of 0.5 mg cm^{-3} of the solutions was chosen. The limiting viscosity number was determined graphically.

Results and discussion

The course of styrene polymerization in the region of low conversions in the polymerization system with two different mass concentrations of ZnO (22.2 g dm$_{em}^{-3}$ and 44.4 g dm^{-3}) was investigated first. The obtained conversion curves are in Fig. 1. It is evident from the figure that in both cases the same induction period was
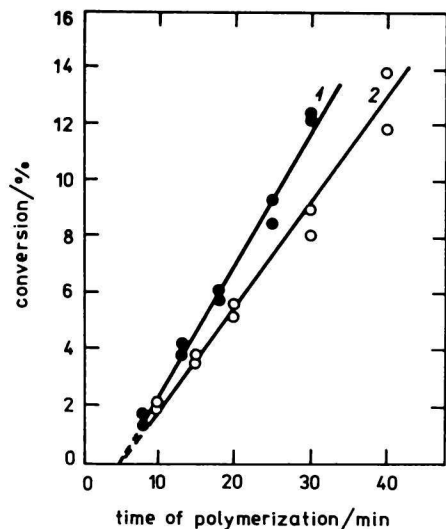

Fig. 1. Conversion curves of emulsion polymerization of styrene at 30 °C with various ZnO concentrations (g dm$_{em}^{-3}$): 1. 44.4, 2. 22.2. Polymerization rate $v_{p1} = 0.44$ conv. % min^{-1}; $v_{p2} = 0.38$ conv. % min^{-1}.
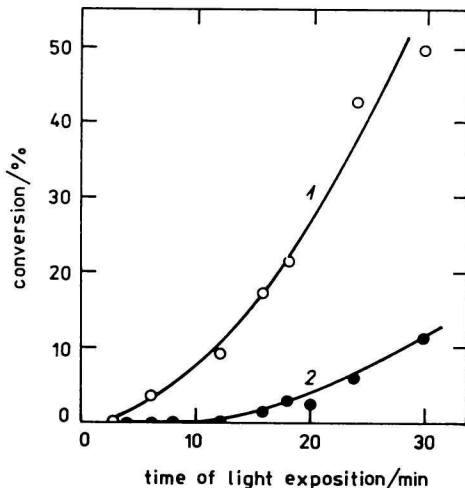
Fig. 2. Dependence of monomer conversion on light exposition time in photoinitiated methyl methacrylate polymerization in the presence of 6.66×10^{-2} mol dm^{-3} ZnO (curve 1) and 2.73×10^{-1} mol dm^{-3} ZnO (curve 2) at 30 °C.

found, which was approximately 5 min. In a similar manner was investigated the influence of the light exposure on the kinetics of methyl methacrylate polymerization during 30 min (the obtained conversion curves are in Fig. 2). The experimental results prove the possibility to use ZnO as a heterogeneous photosensibilizer in the region of visible light for both monomers.

Similarly as for the photoinitiated polymerization of styrene in the presence of the photosensibilizer ZnO, also for the polymerization of methyl methacrylate the induction period is typical. This fact was also proved in the literature [2—4] (even if only traces of water were used) and it can be in connection with the time needed for the sufficient H_2O_2 concentration, the formation of which is supposed in systems containing ZnO, H_2O and traces of oxygen.

During the polymerization of methyl methacrylate a greater induction period was observed, when a higher concentration of ZnO was used, in consequence of which the polymerization rate was lowered. It may be assumed that at higher concentrations of ZnO the content of adsorbed oxygen in the system will be higher, because not all of the oxygen was removed by vacuum; the greater amount of oxygen can take part not only in the formation of hydrogen peroxide but it can markedly act as an inhibitor. In consequence of this the induction period is prolonged by the inhibition period. This may also be indicated by the fact that this phenomenon is not present in the polymerization of styrene, which renders more
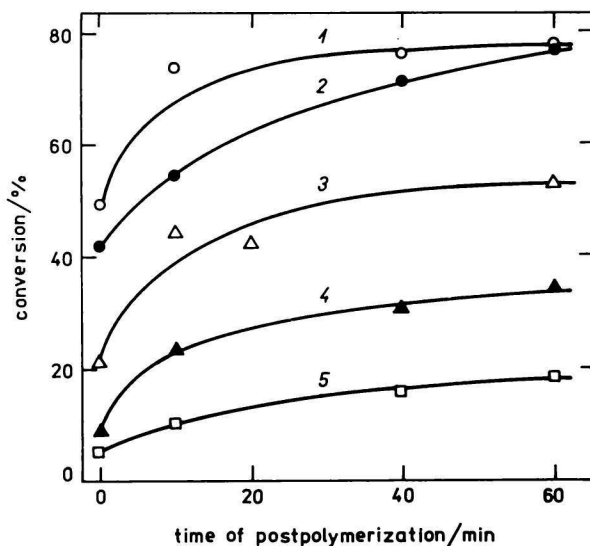

Fig. 3. Dependence of monomer conversion on time of postpolymerization in photoinitiated emulsion polymerization of methyl methacrylate in the presence of 6.66×10^{-2} mol dm^{-3} ZnO at 30 °C at light exposition time/min: *1.* 30; *2.* 24; *3.* 18; *4.* 12; *5.* 6.

stable free radicals, and therefore, less sensitive to the inhibition than methyl methacrylate. Simultaneously also the different polarity of both monomers could be important, which is the reason for the different adsorption ability on the ZnO surface. This could be the cause for the nonlinearity of the conversion curves at methyl methacrylate polymerization in the range investigated, which reflect the enhanced concentration of free radicals caused by the influence of the solid surface. But it is also possible that in the case of higher ZnO concentration in methyl metnacrylate polymerization only the inhibition effect of the greater amount of adsorbed oxygen prevails, whereas, the initiation rate does not increase in consequence of the light scattering by ZnO particles.

Also the course of postpolymerization at different ZnO concentrations in the polymerization system is of interest. The course of the conversion curves of methyl methacrylate postpolymerization during 60 min after the extinction of the light source at five various light exposures in both polymerization systems is in Figs. 3 and 4 At lower ZnO concentration the polymerization is quickly extinct, but at higher ZnO concentration — in spite of the lower polymerization rate during light exposure — the postpolymerization lasts a relatively long time. This is in agreement
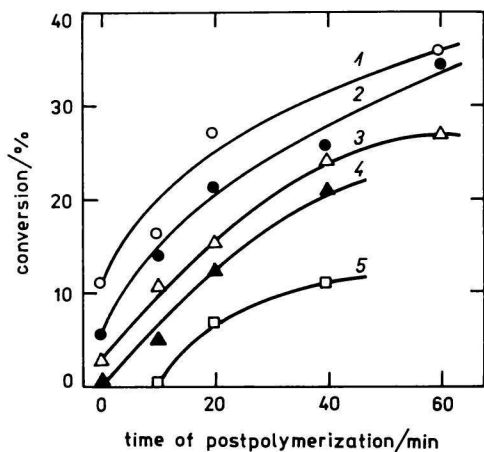

Fig. 4. Dependence of monomer conversion on time of postpolymerization in photoinitiated emulsion polymerization of methyl methacrylate in the presence of 2.73×10^{-1} mol dm^{-3} ZnO at 30 °C for various time of light exposition.
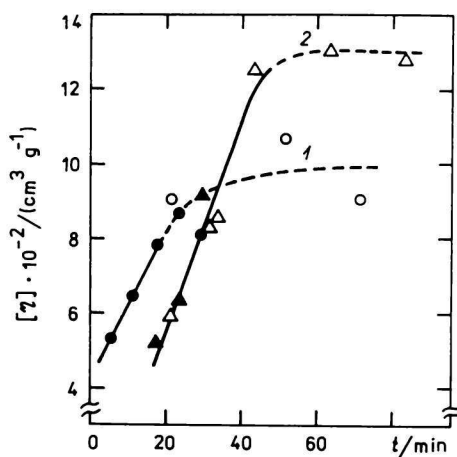
The marking of curves as in Fig. 2.

Fig. 5. Dependence of limiting viscosity number of poly(methyl methacrylate) on the time of emulsion polymerization at 30 °C in the presence of various ZnO concentrations (mol dm^{-3}):

1. 6.66×10^{-2}; 2. 2.73×10^{-1}.

The polymerization during the light exposition is marked by full circles, polymerization with postpolymerization by empty circles.

with the previous statement about the importance of the solid phase in the polymerization system, which is able to contribute to the prolongation of the life of macroradicals and thereby extend the polymer chains.

From the mentioned view-point the molecular characteristics of the formed polymer were important. From the course of the dependence of the limiting viscosity number of samples of poly(methyl methacrylate) on the time of the total polymerization, which is illustrated in Fig. 5, follows more or less the increase and stability of the $\bar{M}_{r,n}$, similarly as the monomer conversion. Molecular characteristics obtained by means of GPC provide an idea about $\bar{M}_{r,w}$ and $\bar{M}_{r,w}/\bar{M}_{r,n}$ of the prepared poly(methyl methacrylate). The results quoted in Table 2 prove the

Table 2

Molecular characteristics of poly(methyl methacrylate) prepared in emulsion polymerization system containing two different ZnO concentrations at 30 °C

ZnO concentration mol dm_{cm}^{-3}	Polymerization time min	$\bar{M}_{r,w} \cdot 10^{-6}$	$\bar{M}_{r,w}/\bar{M}_{r,n}$	Conversion $\alpha/\%$
2.73×10^{-1}	18	9.5	1.93	3.00
	22[a]	11.5	1.55	4.89
	24	9.9	1.73	5.96
	30	11.1	1.52	11.39
	32[a]	12.7	1.44	12.24
6.66×10^{-2}	12	12.3	1.69	9.11
	18	19.6	1.51	21.40
	22[a]	16.1	1.43	23.48
	24	12.2	1.42	42.29
	30	23.9	1.44	49.84

a) During the polymerization the sample was exposed to light for 12 min, the remaining time is the postpolymerization.

increase of the relative molecular mass with the increase of the polymerization time; but the dependence is more unequivocally defined at higher ZnO concentrations in the polymerization system. By increasing the value $\bar{M}_{r,w}$ the ratio $\bar{M}_{r,w}/\bar{M}_{r,n}$ is increased, which becomes stable between 1.4 and 1.5. A mutual comparison of systems with lower and higher ZnO concentration testifies in favour of the system with lower ZnO concentration; at such concentration higher molecular mass of polymers (approximately 2.0×10^7) and lower values of the coefficient of polymolecularity (approximately 1.44) were gained. The results for polystyrene samples, prepared in the presence of various content of ZnO in the polymerization system, obtained by means of GPC are similar (Table 3). It is evident from the

492

table that the relative molecular mass rapidly increased with increasing conversion, but after reaching a relatively low conversion it stabilized or decreased in both polymerization systems with various ZnO content. The coefficient of polymolecularity varied only a little in the studied range and it may be regarded as stable. The mentioned results indicate that this polymerization system with a heterogeneous photosensibilizer like ZnO is very complicated.

Table 3

Molecular characteristics of polystyrene prepared in emulsion polymerization system containing zinc oxide, determined by means of GPC method

ZnO concentration g dm_{cm}^{-3}	Conversion $\alpha/\%$	$\bar{M}_{r.w} \cdot 10^{-6}$	$\bar{M}_{r.w}/\bar{M}_{r.n}$
22.22	1.4	8.57	1.31
	4.0	17.07	1.27
	4.7	25.68	1.33
	14.1	20.65	1.29
	14.6	17.12	1.28
44.44	1.6	11.30	1.32
	2.9	28.42	1.31
	4.1	29.87	1.27
	8.9	26.70	1.34
	12.2	21.18	1.43

Unlike the usual photoinitiated polymerization, the studied emulsion polymerization of styrene and methyl methacrylate requires the presence of an activator, TETA being advantageous. It is not yet possible to characterize unequivocally the initiation mechanism; however it is possible to assume that the activator plays a role in the decomposition of hydrogen peroxide, the formation of which is considered in the literature [2—4] for systems containing ZnO, H_2O, and traces of oxygen or it can itself form initiation centres of polymerization. But TETA can participate also in side reactions where products are formed (stable radicals), which can cause transfer till the termination of radicals. These facts may also explain the decrease of the relative molecular mass of the polymer with polymerization time even at a steady total polymerization rate (in the case of styrene).

The influence of the solid phase (ZnO) in the polymerization system is also significant, which can be a consequence of its semiconducting properties, by which it strongly differs from other studied types of heterogeneous initiators. This assumption may correspond with the fact that with increasing the amount of the light energy quantum the postpolymerization time is also increased.

References

1. Mikulášová, D., Chrástová, V., Citovický, P., and Hudec, I., *Chem. Zvesti 37*, 475 (1983).
2. Kuriacose, J. C. and Markham, M. C., *J. Phys. Chem. 65*, 2232 (1961).
3. Yamamoto, M. and Oster, G., *J. Polym. Sci.*, Part A-1 *4*, 1683 (1966).
4. Seiber, R. P. and Needles, H. L., *J. Appl. Polym. Sci. 19*, 2187, 2206 (1975).
5. Mikulášová, D., Chrástová, V., and Citovický, P., *Eur. Polym. J. 10*, 551 (1974).
6. Chrástová, V., Mikulášová, D., and Citovický, P., *Chem. Zvesti 36*, 223 (1982).
7. *Czech.* 170668 (1974).
8. Benoit, H., Grubisic, Z., Rempp, P., Decker, D., and Zilliox, J. G., *J. Chim. Phys. 63*, 1507 (1966).
9. Tung, L. H., *J. Appl. Polym. Sci. 10*, 375 (1966).
10. Balke, S. T. and Hamielec, A. E., *J. Appl. Polym. Sci. 13*, 1381 (1969).
11. Kotaka, T., *Angew. Makromol. Chem. 56*, 77 (1976).
12. Kotaka, T., *J. Appl. Polym. Sci. 21*, 501 (1977).
13. Chang, V. S. and Huang, R. Y. M., *J. Appl. Polym. Sci. 13*, 1459 (1969).
14. Elias, H. G. and Etter, O., *Makromol. Chem. 66*, 56 (1963).